The Chemistry of the Exploitation of Rare Earths for the Technologies of Today and Tomorrow

The Rare Earths are a group of 17 elements of the Periodic Table, consisting of scandium, yttrium and the 15 lanthanides. They are so called because, despite not being particularly rare in terms of abundance (thulium, the rarest, is 125 times more abundant than gold), [1] they are difficult to extract, and are found in low concentrations within their ores. With the exception of promethium, which is not naturally occurring on Earth, the rare earth metals can be found in the ores monazite and bastnaesite, which primarily contain lanthanum, cerium and neodymium, but traces of all the other elements as well. [2-3]

The rare earth metals have a wide variety of applications in the modern world, resulting from their unique properties such as magnetism, phosphorescence, oxidising power and radioactivity, or lack thereof. The strong permanent magnets that can be made with alloys of neodymium and samarium are used extensively in electronic devices, cerium compounds allow diesel fuels to combust more efficiently, europium helps to prevent forgery, and many have uses in nuclear reactors and medicine. [4]

However, the increasing exploitation of these resources has caused their availability to begin to dwindle, with China, the world's largest provider by far at 90%, predicting that their reserves may run out in as few as 15-20 years. [29] If this is accurate, then it is likely that prices will rise higher and higher as demand outpaces supply, meaning that the world will have find substitutions, or an innovative method of recycling, in order to continue to utilise the lanthanides in the same way as today.

Neodymium magnets and electricity:

Neodymium, when alloyed with iron and boron, can be used to make permanent magnets so strong that two placed near each other will shatter upon collision due to the strength of the attraction. [5] These magnets, in the form $Nd_2Fe_{14}B$, have a remanence (strength of magnetic field that remains once the material that magnetised it has been removed) of up to 1.4T, much higher than the maximum of 0.78T for traditional ferrite magnets. [6] As they are so strong, they have enabled the miniaturisation of many electronic devices, and are used in the generators of wind turbines.

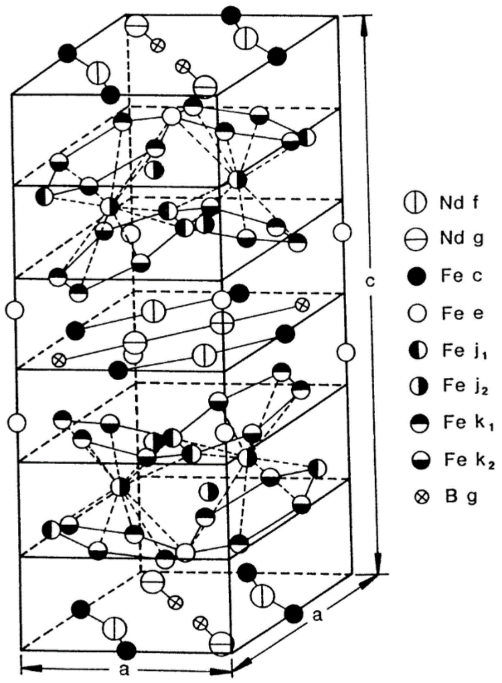


Figure 1 [9]

But how does this magnetism arise? Magnetism occurs due to the presence of unpaired electrons in the outer shells of atoms, where the spin of these electrons creates a minute magnetic effect, which is then magnified when the individual domains become lined up in the presence of a magnetic field, causing the previously random spin orientations to all point in the same direction. [7-8] If the domains remain lined up when the external magnetic field has been removed, then a permanent magnet has been created. Neodymium magnets have such immense strength compared to others as a result of the alloy's complex tetragonal structure, as seen in Figure 1.

$Nd_2Fe_{14}B$ has what is referred to as uniaxial magnetocrystalline anisotropy, meaning that the crystal structure has a unique axis that corresponds with the easy axis of magnetism (the direction inside the crystal along which only a small magnetic field need be applied to reach the saturation magnetism), [10] which is the c-axis, depicted vertically. [11]

These magnets are invaluable in many electronic applications, as their superior strength means that a smaller mass is required in order to achieve the same attractive force, enabling the miniaturisation of devices such as headphones and mobiles. Their strength is also utilised in the generators in wind turbines, where the wind turns the blades, which then turn a rotor that turns a series of (copper) wire coils within the strong magnetic field of a neodymium magnet, inducing an alternating current within the wire, thus generating a current. These permanent magnet generators are favoured by the industry as they do not require an external power supply in order to produce the magnetic field, so they can be used in remote areas with no connection to the grid, and do not require any electricity to function, whilst induction generators do. [12] Although these are currently cost-effective, if demand increases in the future, as it is likely to do, the cost will increase due to the expense and difficulty of the extraction of neodymium and other rare earth metals, which may impact the cost-benefit analysis, and whether production and use of this model will continue into the future.

<u>Phosphorescence- euros and lasers:</u>

If ultraviolet light is shone onto euro notes, the stars shine bright red, and the bridge on the reverse glows green. [13] Although the exact details are kept secret by European banks, the work of Dutch chemists in 2002 revealed that the red light was the result of the presence of europium (III) ions, and the green colour likely arose from the combination of europium ions with others such as strontium, gallium and aluminium, to produce precise spectroscopes that cannot be easily reproduced. [13] the production of the red light from the europium (III) ions occurs when one of the outermost electrons becomes excited due to the UV radiation, and jumps up to a higher energy level. This causes the ion to be unstable, so the electron returns to the lower energy orbital, and the excess energy is emitted as an electromagnetic wave, in this case in the form of visible light with a wavelength of 615nm. [14-15]

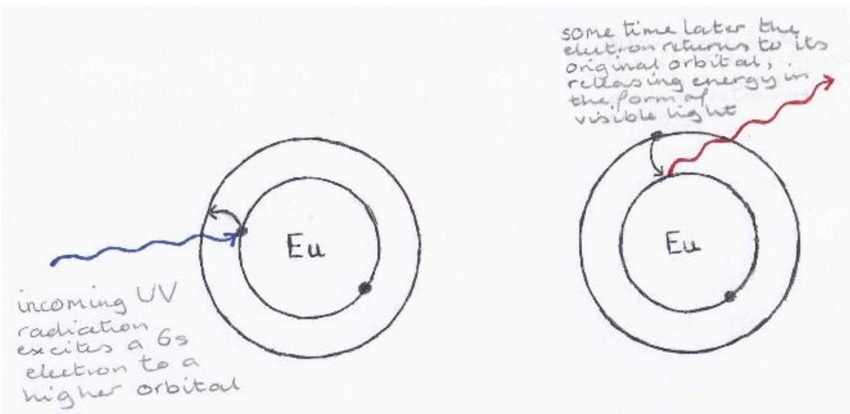


Figure 2

This mechanism of light production also forms the basis for lasers, in which rare earth metals have extensive applications. Different to normal lights, lasers produce a single beam of coherent light all of the same wavelength (due to the excited atoms all being the same element, so producing the same electromagnetic radiation), allowing them to remain focussed for very large distances, and thus giving them varied uses. [25] The most important rare earth laser is the Nd:YAG laser (or Nd:$Y_3Al_5O_{12}$), which is formed by doping the yttrium-aluminium-garnet crystal structure with neodymium (III) ions, which replace some of the yttrium ions due to the similar ionic radius and equal valency. [26] These lasers usually emit in the infrared range, at a wavelength of 1064 nm, but the high-intensity pulse here can be frequency-doubled to achieve a wavelength of 532 nm, which produces a strong green light. [27] They are the most widely used laser in laser-induced thermotherapy, whereby lesions on different organs can be removed, can remove skin cancers, and are used in dentistry for multiple types of soft tissue surgeries. [27] Outside of medicine, they can be used to cut precisely, weld materials together, drill with precision, and for surface modification of materials. [28]

Cerium and diesel:

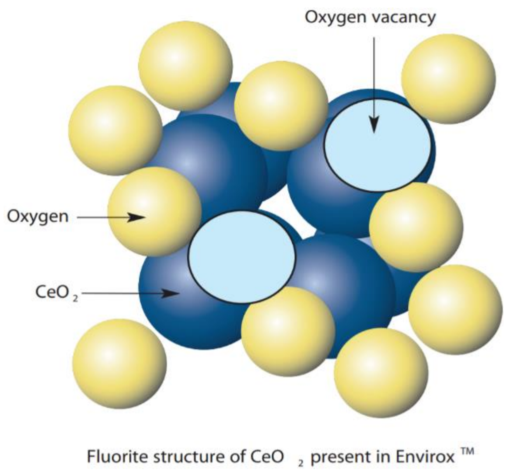


Figure 3 [16]

Cerium is the only one of the rare earth elements to have a stable +4 valency in addition to the usual trivalency of the rest of the lanthanides. [16] This makes it very useful as an oxidising agent, as it can be reduced from +4 to +3, oxidising another species in return. Cerium oxide is frequently used as a catalyst, as the fluorite structure (see Figure 3) remains stable until its melting point of 2600°C, and retains its lattice shape even with the removal of a lot of oxygen and the resultant formation of many oxygen vacancies, meaning that the oxide will not easily decompose. [16] CeO_2 is able to oxidise unburned hydrocarbons such as decane and soot particles, as seen in the following reactions:

$$42CeO_2 + C_{10}H_{22} \rightarrow 21Ce_2O_3 + 5CO_2 + 11H_2O$$

$$4CeO_2 + C \rightarrow 2Ce_2O_3 + CO_2$$

Cerium (III) oxide can then reduce harmful NO_x particles, to nitrogen, also returning itself to cerium (IV) oxide:

$$Ce_2O_3 + NO \rightarrow 2CeO_2 + \tfrac{1}{2} N_2$$ [16]

The addition of nanoparticles of cerium oxide to diesel fuel clearly improves the efficiency and cleanliness of combustion, as harmful emissions are reduced, and build ups of carbon within the combustion chambers of engines can be slowly removed. Although currently this catalysis is a great aid to the car and fuel industries, it is important to question how much longer this will be the case, as diesel vehicles are being phased out in favour of cleaner petrol and electric cars, meaning that cerium oxide may soon no longer be used.

Nuclear reactors:

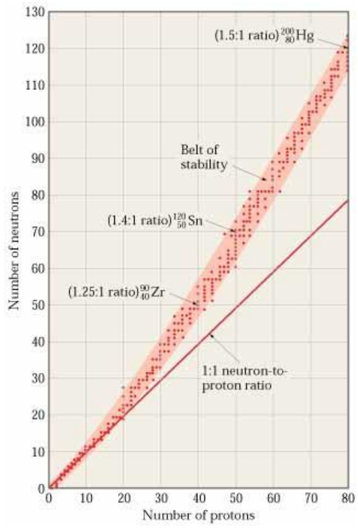


Figure 4 [18]

Most of the lanthanides (from samarium to lutetium) [17] have the ability to absorb neutrons without their nuclei then fissioning themselves, making them ideal elements to use in the control rods of nuclear reactors. This is because their nuclei are large enough that they are able to absorb further nuclei without ending up above the limit of stability shown in the N-Z graph in Figure 4, but not so large that an extra neutron causes them to decay. In addition, each of the lanthanides has multiple stable isotopes, some up to seven, meaning that they can absorb neutrons without any overall effect on the stability of the atom. [19]

Various compositions of different rare earths are used in control rods, such as $Yb_{0.40}$ $Y_{0.27}$ $Lu_{0.12}$ $Er_{0.12}$ $Dy_{0.05}$ $Tm_{0.04}$ $Ho_{0.01}$ from the phosphate mineral xenotite. [17] The lanthanides can then be used in this composition without needing to be separated, as they are all able to absorb neutrons, meaning that they are not very expensive to produce.

Cancer treatment:

The radioactive isotope samarium-153 can be used to relieve pain resulting from bone metastases, and can help treat the cancer, in the form of samarium-153 ethylenediaminetetra(methylenephosphonic acid) (Figure 5), also known by its trade name Quadramet™. [20] This drug is attracted to the calcium cations in hydroxyapatite (Figure 6), which makes up 70% of bone material [21], with the binding being particularly strong in areas of new growth, i.e. the metastases, meaning that the radiation is concentrated around the cancer cells and has no effect on the rest of the body. [22] Once the drug binds to the bone metastases, it is able to treat the pain felt by the patient through the beta decay of the samarium-153 isotope, which decays quickly enough that there is only a negligible amount remaining after twelve hours, reducing the likelihood of any prolonged exposure to potentially hazardous material, thus making this drug safer than others that use isotopes with longer half-lives.

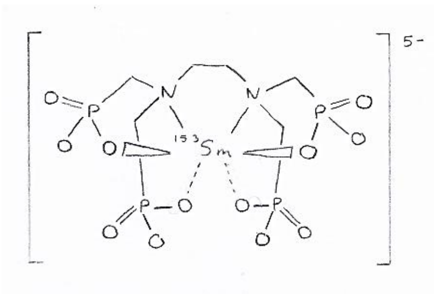
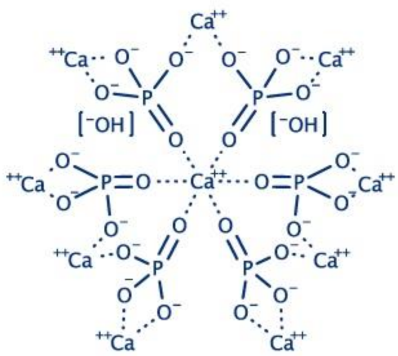


Figure 5 [23]

Figure 6 [24]



What about the future?

It is clear to see that the rare earth metals have a large range of applications in the modern world, which would not function as efficiently without them. Despite this, care must be taken in order to ensure that the resources are not used without necessity, as they are set to increase in scarcity moving into the future. As such, it is likely that the way the elements are used currently will have to be adapted, either to be used more efficiently, or to potentially look for alternatives. It is likely that these developments are already underway, particularly in recycling, but they would not be made available to the public until sufficient research has been carried out.

However, it can be theorised that scientists may be looking into whether cerium oxide can be used in conjunction with petrol fuels, which will be used much further into the future than diesel will. It is also possible that researchers will be able to improve the efficiency of neodymium magnets in order to reduce the amount of the metal used, or reduce the concentration of neodymium by adding other ferromagnetic rare earths into the crystal lattice such as samarium, but due to the importance of these magnets in electrics and the generation of clean energy, it is more likely that savings will have to made elsewhere in order to maintain a good supply of this essential raw material. Ultimately, as with many exploited natural resources, we must use them sparingly, so that tomorrow's planet will be able to utilise them just as the world does today.

Bibliography:

1. http://www.knowledgedoor.com/2/elements_handbook/element_abundances_in_the_earth_s_crust.html [Last accessed 21/01/19]
2. http://www.galleries.com/Bastnasite [Last accessed 20/02/19]
3. http://www.galleries.com/Monazite [Last accessed 20/02/19]
4. http://www.rsc.org/periodic-table/ [Last accessed 20/02/19]
5. https://www.encyclopedia.com/science-and-technology/chemistry/compounds-and-elements/neodymium [Last accessed 24/01/19]
6. http://en.wikipedia.org/wiki/Neodymium_magnet [Last accessed 04/02/19]
7. https://physics.stackexchange.com/questions/75756/on-the-atomic-level-how-do-permanent-magnets-work [Last accessed 20/02/19]
8. https://www.universetoday.com/82049/how-do-magnets-work/ [Last accessed 20/02/19]
9. Nanocrystalline hard magnetic alloys - Scientific Figure on ResearchGate. Available from: https://www.researchgate.net/figure/Tetragonal-unit-cell-of-Nd2Fe14B_fig1_252442554 [Last accessed 20/02/19]
10. https://ocw.mit.edu/courses/materials-science-and-engineering/3-024-electronic-optical-and-magnetic-properties-of-materials-spring-2013/lecture-notes/MIT3_024S13_2012lec25.pdf [Last accessed 20/02/19]
11. https://e-magnetsuk.com/neodymium_magnets/neodymium_magnets_made.aspx [Last accessed 20/02/19]
12. https://www.windpowerengineering.com/electrical/generators/generators/ [Last accessed 21/02/19]

13. Aldersey-Williams, H. (2011) *Periodic Tales*. Great Britain: Penguin Books
14. https://www.britannica.com/science/chemical-analysis/Classical-methods#ref621172 [Last accessed 21/02/19]
15. https://phys.org/news/2005-01-playing-with-light-and-color.html [Last accessed 21/02/19]
16. http://www.energenics.co.uk/wp-content/uploads/Envirox-Catalysis.pdf [Last accessed 22/02/19]
17. https://en.wikipedia.org/wiki/Control_rod [Last accessed 22/02/19]
18. https://socratic.org/questions/how-is-nuclear-stability-related-to-the-neutron-proton-ratio [Last accessed 22/02/19]
19. https://www.britannica.com/science/rare-earth-element/Nuclear-properties [Last accessed 22/02/19]
20. https://www.nps.org.au/australian-prescriber/articles/samarium-sm-153-lexidronam-pentasodium [Last accessed 24/02/19]
21. http://www.c14dating.com/bone.html [Last accessed 24/02/19]
22. https://www.ncbi.nlm.nih.gov/pmc/articles/PMC3407883/ [Last accessed 24/02/19]
23. Redrawn from: https://www.researchgate.net/figure/Chemical-structure-of-153-Sm-EDTMP_fig1_259009668 [Last accessed 24/02/19]
24. https://www.chromspheres.com/nano-hydroxyapatite-powder/ [Last accessed 24/02/19]
25. https://lasers.llnl.gov/education/how_lasers_work [Last accessed 24/02/19]
26. https://www.rp-photonics.com/rare_earth_doped_gain_media.html [Last accessed 24/02/19]
27. https://en.wikipedia.org/wiki/Nd:YAG_laser [Last accessed 24/02/19]
28. http://directedlight.com/ndyag-lasers-industrial-applications/ [Last accessed 24/02/19]
29. http://www.bbc.com/future/story/20140314-the-worlds-scarcest-material [Last accessed 24/02/19]